



TITLE:

On the Synthesis of Alkylphosphonyldichloride

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coating was measured by recording the progressive weight change with a sensitive balance on heating a specimen at temperature of 1050°C. The results are shown in the figure. The curves (1), (2) and (3) are respectively with a specimen of bare metal,

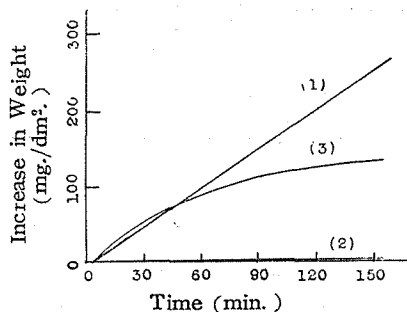


Fig. Effect of addition of vanadium oxide on the oxidation of the base metal.

a specimen covered with enamel containing 10 parts of V_2O_5 to 100 parts of frit and a specimen covered with enamel containing no V_2O_5 . The results indicate clearly that the oxidation of the base metal at high temperature is suppressed by the addition of V_2O_5 to the enamel slip.

10. On the Synthesis of Alkylphosphonyldichloride

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Jensen (*J. Am. Chem. Soc.* **70**, 3880 (1948)) and Soborovskii (*Doklady Akad. Nauk S.S.S.R.* **67**, 293-5 (1949) : *C. A.* **44**, 1401) have recently reported a new method of preparation of organic phosphonyldichloride by blowing oxygen into a mixture of aliphatic or cycloaliphatic hydrocarbon with phosphortrichloride.

The authors have very much interested in these publications and studied this method with higher aliphatic hydrocarbons and examined at the same time the influences of temperature and of the molar ratio of hydrocarbon, phosphortrichloride and oxygen upon the reaction.

Table 1.

No.	Paraffin (g)	PCl_3 (g)	CCl_4 (g)	O_2 (hr)	temp. (°C)	P-contents (%)
1	80	35	100	2	Room temp.	0
2	40	35	0	6	50	0.3
3	20	35	0	12	50	0.69
4	20	52.5	0	12	50	1.13
5	20	35	0	12	75	0.36

In the reaction of paraffin, as given in Table 1, it was found that the reaction did not occur in mild conditions as in the lower hydrocarbons, and that the phosphorous content of the products was increased as the molar ratios of phosphoroustrichloride and of oxygen to the paraffin were increased. Similar result was obtained with liquid paraffin, as given in Table 2.

Table 2.

	Original- compound (g)	PCl ₃ (g)	CCl ₄ (g)	O ₂ (hr)	Temp. (C)	P-contents (%)
Liquid paraffin	22	52.5	0	12	67~70	1.64
Stearic acid	21.4	74.7	0	12	70~75	4.17

Then, with stearic acid and cetylalcohol some experiments were performed to see the influence of carboxyl group upon the reactivity of the hydrocarbon chain.

One of the data is given in Table 2.

The results show that the carboxyl group activates the paraffin chain to some degree. For the reaction of cetylalcohol the result is not given because the analysis was confused by the formation of cetyl-alcoholmonophosphoric acid ester.

The isolation of the paraffin phosphonic acid in pure state from the reaction mixture was so difficult that the products which has a purity higher than 50 % could not be obtained, but the product was found to be the expected paraffin phosphonic acid by means of the formation of alkali salts.

In the case of liquid paraffin, phosphonyldichloride was treated with glycerin in the presence of pyridin and the corresponding diglyceride was obtained; the phosphor content of this diglyceride was analysed and found to be 5,11 % (calculated value 5,48 %).

Conclusion.

The authors have ascertained that this synthetic method can be applied to higher hydrocarbons in proper conditions, although the yield of the phosphonyldichloride is not so high and the purification procedure is not easy.

11. On the Transjointing Reactions of Jointed Compounds

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Introduction

The condensation of two passive components (P₁H and P₂H) with formaldehyde